Reactions of 1,4-benzoquinones with s^2 reducing centers†

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Aqueous solutions of Sn(II) and Ge(II) (in chloride media) and In(I) (in perchlorate media) react quantitatively with 1,4-benzoquinone and its 2,5-$(OH)_2$ and 2,5-Cl_2-3,6-$(OH)_2$ derivatives, reducing the oxo-functions to 1,4-$(OH)_2$. For Sn(II) and Ge(II), reaction is accelerated by incorporation of 2,5-$(OH)_2$ substituents and by chloroanation of the s^2 center. The most reactive reducing Sn(II) species are $SnCl_3^-$ for benzoquinone and dihydroxyquinone but $SnCl_2(aq)_x$ for the dichloroquinone. Reductions by Ge(II) proceed mainly through a species (probably $GeCl_4^{2-}$) having one more chloride than the predominant form. The activated complex for the $(OH)_2$bzq–Ge(II) reaction features two germanium centers, only one of which is involved in the reduction act. Reductions of these quinones by In(I) proceed 10^2–10^3 times as rapidly as those by Sn(II) and Ge(II) and are not accelerated by hydroxylation of the quinone ring.

Introduction

Quinones assume essential functions in a multitude of biological redox systems. They exhibit chemical and structural versatility enabling them to act, depending on conditions, as hydrogen atom acceptors, as single-, and as two-electron acceptors. The ability of isopreinoid-substituted quinones to transfer reducing equivalents across a membrane is reflected in their central role in energy metabolism.[2] Quinones, in addition, are versatile oxidizing and dehydrogenating agents in the organic laboratory,[3a] and, with suitable structural modification, may feature significant herbicidal, antibiotic, or antineoplastic activity.[3b]

The present study deals with the reactions of water-soluble quinones [1,4-benzoquinone and its 2,5-$(OH)_2$- and 2,5-Cl_2-3,6-$(OH)_2$-substituted derivatives, **I** and **II**] with s^2 metal-ion reducing centers, two of which, indium(I)[4] and germanium(II)[5] have recently become available in readily workable concentrations. Since these reductants, like quinones, can enter into both $1e^-$ and $2e^-$ transactions, several mechanistic possibilities are conceivable. In examining eight separate quinone + s^2 redox systems we find no fewer than seven different rate laws.
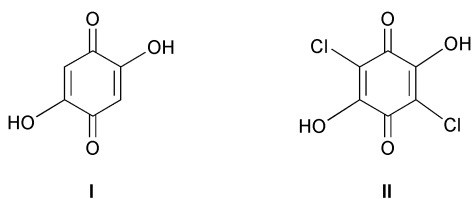
Experimental

Materials

All solutions were prepared using Millipore-Q-treated deionized water that had been boiled for 2 h and then purged with high purity argon for 2 h more to remove dissolved oxygen. Germanium(IV) oxide, tin(II) chloride, indium metal powder, silver trifluoromethanesulfonate (silver triflate), and quinones (Aldrich products) were used as received. Solutions of indium(I) triflate were prepared by the method of Chandra,[6] and solutions of germanium(II) were generated and analyzed as described by Babich.[5] Tin(II) solutions were prepared by dissolving 0.60–1.0 g of $SnCl_2$ in 6–8 ml of air-free aqueous

Table 1 Stoichiometries of the reactions of 1,4-quinones with s^2 metal-ion reducing centers[a]

Quinone	Reductant	Δ[Quinone]/Δ[reductant]
Benzoquinone[b]	Ge^{II}	0.94 ± 0.01
	Sn^{II}	0.94 ± 0.02
	In^{I}	0.99 ± 0.01
2,5-Dihydroxybenzoquinone[c]	Ge^{II}	0.96 ± 0.02
	Sn^{II}	1.00 ± 0.06
	In^{I}	0.94 ± 0.03
2,5-Dichloro-3,6-dihydroxy-benzoquinone[d] (chloranilic acid)	Ge^{II}	0.95 ± 0.01
	Sn^{II}	1.04 ± 0.03
	In^{I}	0.94 ± 0.02

[a] Reactions were carried out at 22 °C in 0.3 M HCl (Ge^{II} and Sn^{II}) or 0.3 M $HClO_4$ (In^{I}). Reductant was taken in 30–80% deficiency. [b] λ = 247 nm. [c] λ = 283 nm. [d] λ = 305 nm.

solutions 0.5 M in HCl and 1.0 M in NaCl, then centrifuging. The clear supernatant was analyzed by titration with KI_3 at 353 nm and kept under argon.

Stoichiometric studies

Stoichiometric determinations were carried out under argon and monitored at λ_{max} of the oxidizing quinone. Measured deficient quantities of each reductant were added to a known excess of the oxidant. Decreases in absorbance were compared with those resulting from excess reductant. Results are summarized in Table 1.

Kinetic studies

Reactions were carried out under argon. Rates were evaluated from absorbance decreases at λ_{max} of the oxidant, using either a Shimadzu 1601 instrument or a Durrum–Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 22.0 ± 0.5 °C. Ionic strength was maintained by addition of HCl–NaCl–NaClO$_4$. Pseudo-first order conditions were used, with the concentration of the reagent in excess varying by less than 10% during the course of a run. Rate constants were evaluated by nonlinear least-squares fit to the relationship describing exponential decay. All reactions were first order in quinone, and all but one (see Results) were first order in reductant as well. No distortion of kinetic curves indicative of the growth or decay of a reaction intermediate on a time scale similar to that of the primary reaction was observed.

† Electron transfer, Part 155.[1]

Table 2 Kinetic data for reduction of 1,4-quinones with tin(II)[a]

A. Benzoquinone[b]			B. 2,5-(OH)$_2$bzq[c]			C. 2,5-Cl$_2$-3,6-(OH)$_2$bzq[d]		
[H$^+$]/M	[Cl$^-$]/M	k_2/M^{-1} s^{-1}	[H$^+$]/M	[Cl$^-$]/M	$10^{-2}\,k_2$/M^{-1} s^{-1}	[H$^+$]/M	[Cl$^-$]/M	$10^{-1}\,k_2$/M^{-1} s^{-1}
0.10	0.10	0.34 (0.23)	0.20	0.20	0.45 (0.45)	0.050	0.50	5.9 (5.8)
0.10	0.20	1.15 (0.96)	0.20	0.30	0.63 (0.63)	0.10	0.50	5.4 (5.0)
0.10	0.30	1.67 (1.86)	0.20	0.50	0.97 (0.96)	0.25	0.50	3.8 (3.6)
0.10	0.40	2.5 (2.7)	0.20	0.70	1.28 (1.28)	0.30	0.50	3.7 (3.4)
0.10	0.50	3.5 (3.5)	0.20	0.80	1.40 (1.42)	0.40	0.50	3.2 (3.0)
0.17	0.50	3.8 (4.0)	0.20	0.90	1.49 (1.56)	0.50	0.50	2.8 (2.7)
0.20	0.50	4.3 (4.2)	0.20	1.00	1.68 (1.69)	0.20	0.11	1.41 (1.47)
0.30	0.50	4.6 (4.9)	0.50	1.00	1.74 (1.69)	0.20	0.21	2.3 (2.8)
0.40	0.50	5.6 (5.5)	1.00	1.00	1.65 (1.69)	0.20	0.31	2.9 (3.5)
0.50	0.50	6.2 (6.2)				0.20	0.41	3.4 (3.9)
						0.20	0.50	3.5 (4.0)

[a] Reactions were carried out under pseudo-first order conditions at 22.0 ± 0.5 °C; [quinone] = (2.0–5.0) × 10^{-5} M; [Sn^{II}] = (0.6–1.8) × 10^{-3} M. [b] μ = 0.5 M (HCl/NaCl/HClO$_4$), 247 nm; parenthetical rates (right hand column) were calculated using eqn. (3) and parameters from Table 5. [c] μ = 1.0 M, 280 nm; parenthetical rates calculated using eqn. (7) and parameters from Table 5. [d] μ = 0.5 M, 305 nm; parenthetical rates calculated from eqn. (8) and parameters from Table 5.

Results

The close approach to 1 : 1 stoichiometry observed for all reactions examined (Table 1), in conjunction with the absence of spectral features attributable to a semiquinone, points to a relatively clean reduction to a hydroquinone in each case:

(1)

(2)
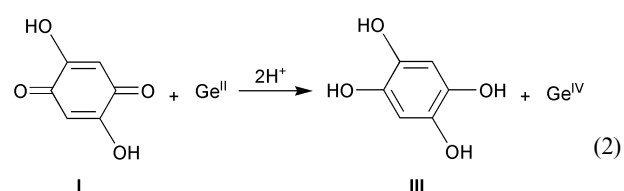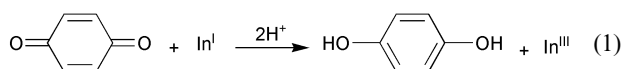
Analogous reductions of quinone **I** to tetrol **III**, using tin metal have been reported.[7]

Although the net reaction is the same in all instances, the kinetic picture features remarkable variation. At one extreme, the very rapid In(I) reductions of benzoquinone ($k = 8.9 \times 10^4$ M^{-1} s^{-1}) and its 2,5-(OH)$_2$ derivative (3.2×10^4 M^{-1} s^{-1}) exhibit straightforward second order behavior with no acidity dependence in the range 0.01–0.50 M H$^+$.
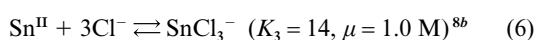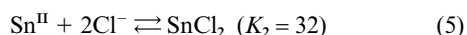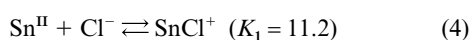
Reductions with Sn(II)

The Sn(II) and Ge(II) reaction mixtures contain chloride since both of these reductants are prepared in strong HCl.[5] Reductions with these centers may exhibit [Cl$^-$]- or [H$^+$]-dependencies or both. Data for Sn(II) are assembled in Table 2.

Rates for the Sn(II)–benzoquinone reaction conform to expression (3)

$$k_{\text{obsd}} = \frac{-\mathrm{d}[\text{bzq}]/[\mathrm{d}t]}{[\text{bzq}][\text{Sn}^{II}]} = \frac{(k_3 + k_3^{H}[\text{H}^+])K_3[\text{Cl}^-]^3}{1 + K_1[\text{Cl}^-] + K_2[\text{Cl}^-]^2 + K_3[\text{Cl}^-]^3}$$

(3)

The four term denominator in (3) (abbreviated D) often occurs in rate laws associated with reactions of Sn(II) in chloride media[8] and reflects partition of this reductant into four ligation levels[9]

$$\text{Sn}^{II} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+ \quad (K_1 = 11.2)$$

(4)

$$\text{Sn}^{II} + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_2 \quad (K_2 = 32)$$

(5)

$$\text{Sn}^{II} + 3\text{Cl}^- \rightleftharpoons \text{SnCl}_3^- \quad (K_3 = 14, \mu = 1.0\ \text{M})^{8b}$$

(6)

Rate law (3) indicates that this reduction occurs *via* competing protonated and non-protonated (k_3) paths, both involving the trichloro reductant, SnCl$_3^-$. Refinement of data in terms of (3) yields rate constants 8.3 ± 0.6 M^{-1} s^{-1} for the k_3 path and 19 ± 3 M^{-2} s^{-1} for the protonated component. Alternate sequences involving the lower chloro complexes of Sn^{II} as well did not improve the fit. Calculated and observed rates are compared on the right-hand column of the benzoquinone entries.

The 2,5-dihydroxy oxidant reacts much more rapidly than its parent quinone and exhibits a substantially altered kinetic profile. Rates vary according to eqn. (7).

$$k_{\text{obsd}} = \frac{k_1 K_1[\text{Cl}^-] + k_2 K_2[\text{Cl}^-]^2 + k_3 K_3[\text{Cl}^-]^3}{D}$$

(7)

The "speciation denominator", D is again there, but no [H$^+$]-dependent contribution is noted. Moreover, there are minor but perceptible contributions involving SnCl$^+$ and SnCl$_2$. Refinement yields: $k_1 = 39 \pm 8$ M^{-1} s^{-1}, $k_2 = (5 \pm 1) \times 10$ M^{-1} s^{-1}, and $k_3 = (5.7 \pm 0.3) \times 10^2$ M^{-1} s^{-1}.

Unlike the parent quinone, the (OH)$_2$Cl$_2$-substituted oxidant is reduced with Sn(II) in a reaction retarded by increase in acidity. The redox burden in this instance is carried by SnCl$_2$, but partition into two paths at different protonation levels requires inclusion of an [H$^+$]-dependent "partition ratio" in the rate law (8)

$$k_{\text{obsd}} = \frac{K_2[\text{Cl}^-]^2}{D} \frac{(k_2 K_{\text{HA}} + k_2^{H}[\text{H}^+])}{(K_{\text{HA}} + [\text{H}^+])}$$

(8)

where k_2 and k_2^{H} pertain to the deprotonated and protonated paths and K_{HA} is the acidity constant governing the conversion. Refinement of data based on (8) yields $k_2 = (2.2 \pm 0.1) \times 10^2$ M^{-1} s^{-1}, $k_2^{H} = 35 \pm 9$ M^{-1} s^{-1}, and $K_{\text{HA}} = 0.18$ M. As expected, the rate constant for the deprotonated contribution exceeds that for the protonated.

Reductions with Ge(II)

Data for Ge(II) reductions of benzoquinone and its dichloro-dihydroxy derivative appear in Table 3. Rate laws for both oxidants, (9) and (10), feature the denominator (1 + K[Cl$^-$]), which may be taken to reflect the partition of reductant between a principal and a subsidiary complex, the latter with one additional chloride.

$$\text{for bzq: } k_{\text{obsd}} = \frac{k_\text{o} + k_1 K[\text{Cl}^-]}{1 + K[\text{Cl}^-]}$$

(9)

Table 3 Kinetic data for reduction of 1,4-quinones with Ge(II) [a]

A. Benzoquinone [b]			B. 2, 5-Cl$_2$-3,6-(OH)$_2$bzq [c]		
[H$^+$]/M	[Cl$^-$]/M	$10^{-2}\,k_2$/M^{-1} s^{-1}	[H$^+$]/M	[Cl$^-$]/M	$10^{-2}\,k_2$/M^{-1} s^{-1}
0.10	0.10	0.37 (0.36)	0.10	0.50	0.58 (0.53)
0.10	0.15	0.50 (0.48)	0.20	0.50	1.07 (1.07)
0.10	0.20	0.58 (0.59)	0.30	0.50	1.63 (1.60)
0.10	0.25	0.62 (0.71)	0.40	0.50	2.10 (2.14)
0.10	0.30	0.81 (0.82)	0.50	0.50	2.6 (2.7)
0.10	0.40	1.05 (1.03)	0.20	0.033	0.47 (0.48)
0.10	0.45	1.17 (1.14)	0.20	0.10	0.57 (0.57)
0.10	0.50	1.34 (1.24)	0.20	0.15	0.67 (0.64)
0.20	0.50	1.33 (1.24)	0.20	0.20	0.70 (0.70)
0.40	0.50	1.33 (1.24)	0.20	0.30	0.79 (0.83)
0.50	0.50	1.30 (1.24)	0.20	0.40	0.93 (0.95)
			0.20	0.45	1.08 (1.01)

[a] For the 2,5-(OH)$_2$bzq–Ge(II) systems, which exhibits second order reductant dependency see Table 4. The reactions above were monitored under pseudo-first order conditions at 22.0 ± 0.5 °C; [quinone] = (2.0–3.0) × 10^{-5} M; [Ge^{II}] = (0.5–3.2) × 10^{-3} M. [b] μ = 0.5 M (HCl/NaCl/HClO$_4$), λ = 247 nm; parenthetical rates were calculated using eqn. (9) and parameters from Table 5. [c] λ = 305 nm; parenthetical rates were calculated using eqn. (10) and parameters from Table 5.

Table 4 Reduction of 2,5-dihydroxybenzoquinone with germanium(II) [a]

[H$^+$]/M	[Cl$^-$]/M	10^4[Ge^{II}]/M	k_{obsd}/s^{-1}
0.30	1.00	7.00	2.6 (2.7)
0.50	1.00	7.00	1.74 (1.62)
0.80	1.00	7.00	1.14 (1.02)
1.00	1.00	7.00	0.92 (0.81)
0.50	0.50	8.00	1.20 (1.21)
0.50	0.60	8.00	1.49 (1.43)
0.50	0.70	8.00	1.60 (1.62)
0.50	1.00	8.00	1.92 (2.12)
0.50	1.00	2.20	0.13 (0.16)
0.50	1.00	6.80	1.21 (1.53)
0.50	1.00	9.00	2.69 (2.69)
0.50	1.00	13.5	6.2 (6.0)
0.50	1.00	18.0	11.9 (10.7)
0.50	1.00	30.0	29.8 (29.8)

[a] Reactions were carried out under pseudo-first order conditions at 22.0 ± 0.5 °C; [quinone] = (2.0–5.0) × 10^{-5} M. [b] μ = 1.0 M (HCl/NaCl/HClO$_4$; λ = 280 nm; parenthetical rates calculated using eqn. (11) and parameters from Table 5.

$$\text{for Cl}_2(\text{OH})_2\text{bzq: } k_{obsd} = \frac{(k_o + k_1 K[\text{Cl}^-])[\text{H}^+]}{1 + K[\text{Cl}^-]} \quad (10)$$

Refinements yield k_1 = (1.25 ± 0.07) × 10^2 M^{-1} s^{-1} and k_o = 12 ± 3 M^{-1} s^{-1} for benzoquinone and k_1 = (3.7 ± 0.1) × 10^3 M^{-2} s^{-1} and k_o = (2.2 ± 0.1) × 10^2 M^{-2} s^{-1} for the dichloro oxidant.

Unlike its unsubstituted parent, the dichloroquinone is reduced predominantly through protonated forms. The protonations required for activation must involve an acid center with a pK value well below zero since there is no hint of kinetic saturation involving [H$^+$]. If the pK_A of the protonated quinone is assumed to lie near the documented value, −6,[10] bimolecular rate constants for these highly acidic forms (featuring the function >C=OH$^+$) fall in the range 10^8–10^9 M^{-1} s^{-1}.

Data for the Ge(II) reduction of 2,5-(OH)$_2$bzq are summarized in Table 4. Observed accelerations with added reductant are clearly more steep than that corresponding to a proportional relationship. Rate law (11), which correlates these data,

$$k_{obsd} = \frac{\text{d[bzq]/d}t}{[\text{bzq}]} = \frac{kK_1[\text{Cl}^-][\text{Ge}^{II}]^2}{[\text{H}^+](1 + K_1[\text{Cl}^-])^2} \quad (11)$$

again includes a denominator indicating partition of Ge(II) and points to preponderant activated complex having two units of Ge(II) and a single Cl$^-$ with one proton removed (presumably

from a hydroxy group of the oxidant) Refinement (keeping K_1 as 0.2) yields k = (9.9 ± 0.1) × 10^6 M^{-1} s^{-1}.[11] Rate laws and kinetic parameters are summarized in Table 5.

Discussion

Kinetic profiles of these quinone reductions exhibit no irregularities pointing to the formation or decay of a semi-quinone intermediate on a time scale comparable to that of the principal conversions. We may then infer either that two electrons are transferred from the donor center in a single transaction, or that if a pair of single electron transfers are involved, rates are determined by the initial act, followed by a rapid (and kinetically silent) follow-up step.

The Franck–Condon barrier to outer sphere 2e$^-$ transfers is generally taken to be prohibitively high,[12] but the structure of our oxidants allows initiation via metal–carbonyl coordination (12), after which internal electron transfer within the ^{II}M(bzq) complex (13) yields the dihydroxy product.

$$\text{M}^{II} + \text{bzq} \rightleftarrows \text{M}^{II}:\text{bzq} \quad (12)$$

(13)
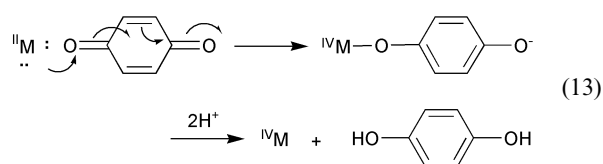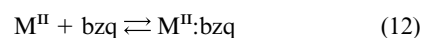
Although the general sequence (12)–(13) may apply to all redox systems here examined, differences in the detailed behavior of Sn(II) and Ge(II) in solution can elaborate the resulting rate laws. The denominators of each of the three Sn(II) reactions mirror the known speciation[9] of Sn(II) in aqueous chloride. In addition, the Sn(II)–bzq reaction [eqn. (3)] receives a modest kinetic boost from H$^+$ and a much more dramatic push from tris-anation of the reductant (the [Cl$^-$]^3 dependence). The K_3^H [H$^+$] contribution doubtless arises from partial protonation of the oxidant, which would be expected to ease internal electron transfer within the M^{II}(bzq) complex. The [Cl$^-$]^3 proportionality brings to mind similar dependances observed for Sn^{II} reactions which are presumed to proceed through Sn^{III},[8b,13] and leads us to wonder whether the internal transfer (13) takes place in a single act or in a pair of 1e$^-$ steps.

The Ge(II)–bzq reaction, involving a much stronger reductant ($E^0_{IV,II}$ = −0.22 V at pH 0), requires only partial help from a [Cl$^-$]^1-assisted path [eqn. (9)] and no protonation. The two-term denominator indicates that Ge(II) in the systems at hand exists

| Reductant	Oxidant	Rate law	Eqn. no.	Parameters
Sn(II)	Benzoquinone	$$\dfrac{[ox][red](k_3 + k_3^H\,[H^+])K_3[Cl^-]^3}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$$	(3)	$k_3^H = 19 \pm 3\ M^{-2}\ s^{-1}$ $k_3 = 8.3 \pm 0.6\ M^{-1}\ s^{-1}$ $K_1 = 11.2,\ K_2 = 26,\ K_3 = 55$
	(OH)$_2$bzq[b]	$$\dfrac{[ox][red](k_1 K_1[Cl^-] + k_2 K_2[Cl^-]^2 + k_3 K_3[Cl^-]^3)}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$$	(7)	$k_1 = 39 \pm 8\ M^{-1}\ s^{-1}$ $k_2 = (5 \pm 1) \times 10\ M^{-1}\ s^{-1}$ $k_3 = (5.7 \pm 0.3) \times 10^2\ M^{-1}\ s^{-1}$
	Cl$_2$(OH)$_2$bzq	$$\dfrac{[ox][red]K_2[Cl^-]^2(k_2 K_{HA} + k_2^H\,[H^+])}{(1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3)(K_{HA} + [H^+])}$$	(8)	$k_2 = (2.2 \pm 0.1) \times 10^2\ M^{-1}\ s^{-1}$ $k_2^H = 35 \pm 9\ M^{-1}\ s^{-1}$ $k_{HA} = 0.18$
Ge(II)	Benzoquinone	$$\dfrac{[ox][red](k_o + k_1 K[Cl^-])}{1 + K[Cl^-]}$$	(9)	$k_o = 12 \pm 3\ M^{-1}\ s^{-1}$ $k_1 = (1.25 \pm 0.07) \times 10^2\ M^{-1}\ s^{-1}$ $K = 0.20$
	(OH)$_2$bzq[b]	$$\dfrac{[ox][red]^2 kK[Cl^-]}{[H^+](1 + K[Cl^-])^2}$$	(11)	$k = (9.9 \pm 0.1) \times 10^6\ M^{-1}\ s^{-1}$ $K = 0.20$
	Cl$_2$(OH)$_2$bzq	$$\dfrac{[ox][red][H^+](k_o + k_1 K[Cl^-])}{1 + K[Cl^-]}$$	(10)	$k_o = (2.2 \pm 0.1) \times 10^2\ M^{-2}\ s^{-1}$ $k_1 = (3.7 \pm 0.1) \times 10^3\ M^{-2}\ s^{-1}$
In(I)	Benzoquinone	$k[ox][red]$		$k = (9.4 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$
	(OH)$_2$bzq	$k[ox][red]$		$k = (3.1 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1}$

[a] Reactions at 22.0 ± 0.5 °C, μ = 0.5 M unless otherwise indicated. Supporting electrolyte was (HCl/NaClO$_4$/HClO$_4$) for Sn(II) and Ge(II) reactions, (HClO$_4$/NaClO$_4$) for In(I) reactions. [b] μ = 1.0 M.

primarily as two species differing by a single chloride. Quantitative data concerning speciation of Ge(II) at high [Cl⁻] are scarce, but Poshkozim[14] has presented evidence that the predominant form in 0.1–0.5 M HCl is GeCl$_3^-$. Data are then consistent with equilibrium (14)

$$GeCl_3^- + Cl^- \rightleftharpoons GeCl_4^{2-} \qquad (14)$$

for which the modest equilibrium constant 0.20 ± 0.02 has been recorded.[8a]

The proverbial electron-donating capabilities of aryl-bound hydroxy substituents would be expected to disfavor acceptance of external electrons by the quinone. For the systems at hand, however, incorporation of hydroxy groups in the unit greatly facilitates reduction. We suspect that chelation has entered the picture here, with formation of a cyclic intermediate (*e.g.* **IV**),


IV
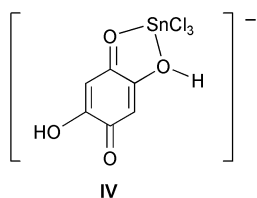
thus increasing the concentration of this precursor complex. It is likely that the predominant k_3 path for the (OH)$_2$bzq–Sn(II) reaction [eqn. (7)] utilizes chelation, but this is less certain for the marginal k_1 and k_2 paths.

The enhanced acidity of the Cl$_2$(OH)$_2$-substituted quinone comes into play in its reduction by Sn(II) [eqn. (8)]. Here, virtually every act of reduction involves the dichloro reductant but the familiar kinetic acidity dependence corresponds to partition into a deprotonated path (k_2) and a protonated component (k_2^H). Of the two precursors, the protonated is evidently

more thinly populated. Hence in this case, reaction is favored at lower acidities. Why a similar partition of paths is not observed in Ge(II) reduction of the same quinone [eqn. (10)] remains a puzzling point.

The most unusual kinetic behavior in this series is encountered with the (OH)$_2$bzq–Ge(II) system. The reaction is very nearly *second* order in reductant (in the range 0.2–3.0 mM) although the observed stoichiometry lies close to 1 : 1 (Table 1). In addition, there is a [Cl⁻]-dependence and a 1/[H⁺] proportionality. The implied activated complex, consisting of a unit of quinone (from which one H⁺ has been removed), two germaniums, and one chloride, is consistent with Scheme 1.

Here, we suggest that the role of the second (non-oxidized) Ge^{II} is simply as a positive center [analogous to H⁺ in the Sn(II) reductions] which may facilitate electron flow from the active Ge(II)–Cl through the ring system.
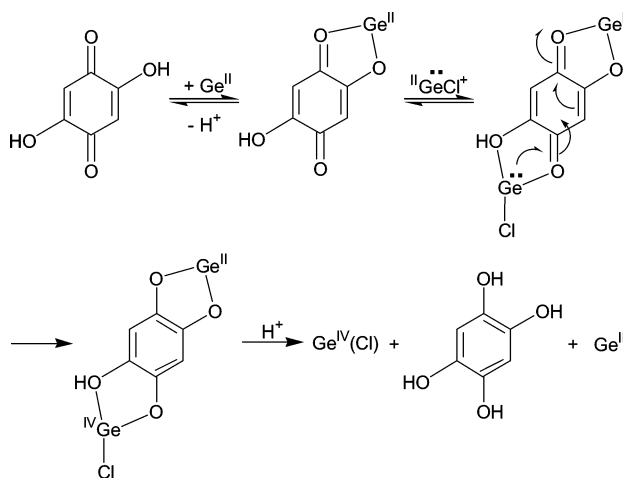
Scheme 1

The very high rates (10^4–10^5 M^{-1} s^{-1}) and simple monomial rate laws for reductions by In(I) hint at a change of mechanism for this donor. Moreover, incorporation of 2,5-$(OH)_2$ substituents is seen to retard, rather than accelerate reaction, indicating that chelation plays no appreciable part with this unipositive center. The difference brings to mind the recognized redox versatility of In(I). Although normally a $2e^-$ reagent, it can reduce single electron oxidants, utilizing both bridged[6] and outer-sphere[15] routes. In this case, the lack of kinetic response to ring substituents leads us tentatively to favor initiation by an outer-sphere single electron transfer to the quinone, yielding a semiquinone radical and In^{2+}. Subsequent reaction of these two unstable species must be very rapid (possibly geminate recombination) since we see no distortions of kinetic profiles attributable to their intervention.

Conclusions

The bewildering array of rate laws describing the Sn(II) and Ge(II) reductions of the quinones examined, (reflecting, in part, differing speciation behavior of the donors) should not obscure similarities pertaining to the systems. Our evidence is consistent with reactions occurring by two-unit inner-sphere transactions, with conversions particularly with Sn(II), by polychloro anation of the reductant.

The picture with regard to In(I) reductions is less clear, but the marked differences in observed patterns serve to remind us that for this donor, the possibility of reaction *via* successive single electron steps should not be ignored.

Acknowledgements

References and notes

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